Enhanced Solubility of Silica and Accelerated Fluid-Silicate Reaction Rates in an Experimental Supercritical Carbon Dioxide-Brine-Rock System

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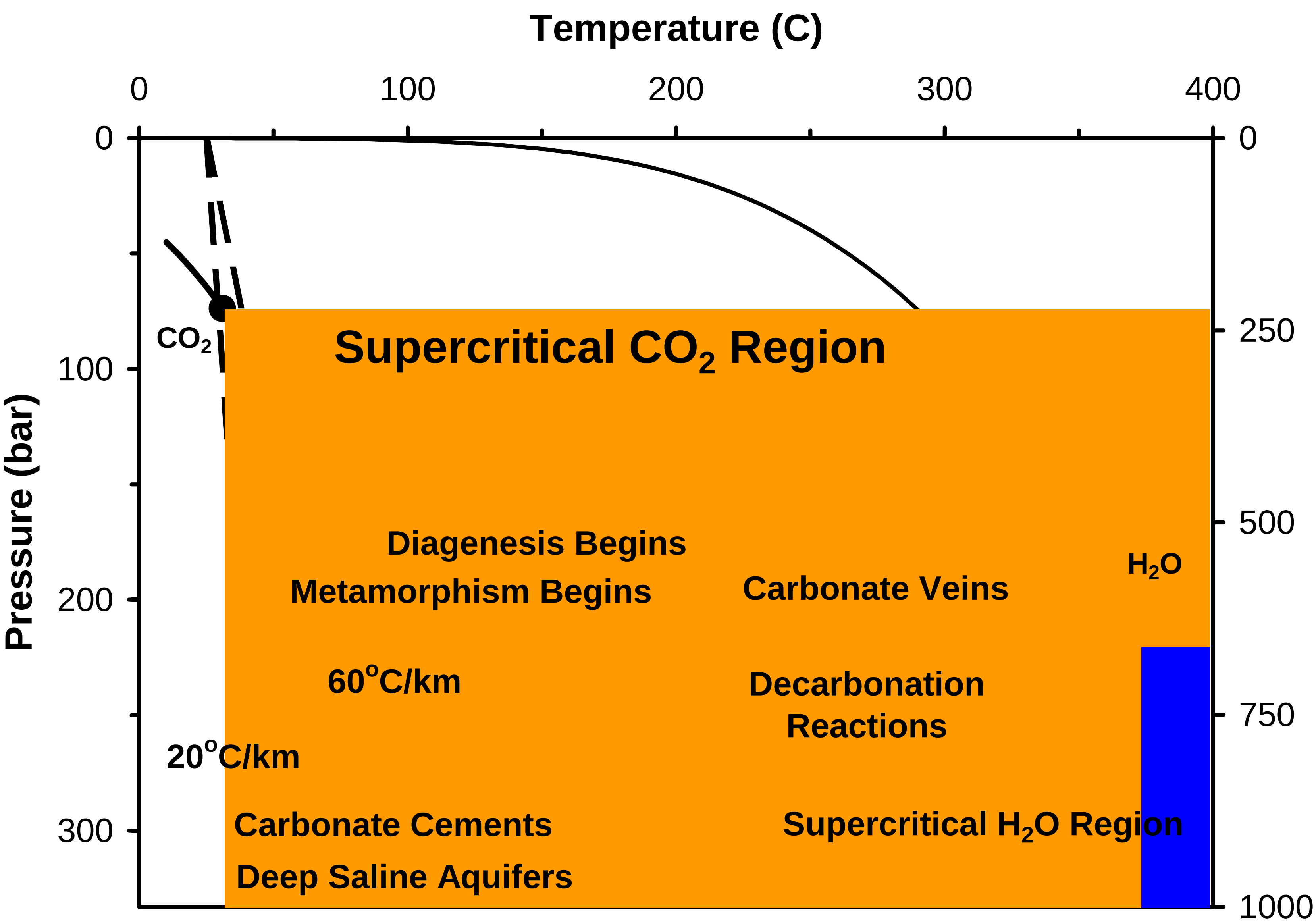
Background

The potential significance of two fluid phases (excluding air and hydrocarbons) has been established for a limited number of geochemical processes.

- **Phase equilibria in metacarbonate rocks for low to moderate prograde metamorphism (*e.g*., Bowers and Helgeson, 1983)**
- **Flow and transport in metamorphic rocks (Yardley and Bottrell, 1988)**
- **Fluid inclusions (various authors)**

Supercritical Regions for CO_2 and H_2O



Hypothesis

Reactive properties of a supercritical CO_2 phase that may coexist with brine at low T and P has not been evaluated or appreciated for a broader range of geologic systems. Potential examples:

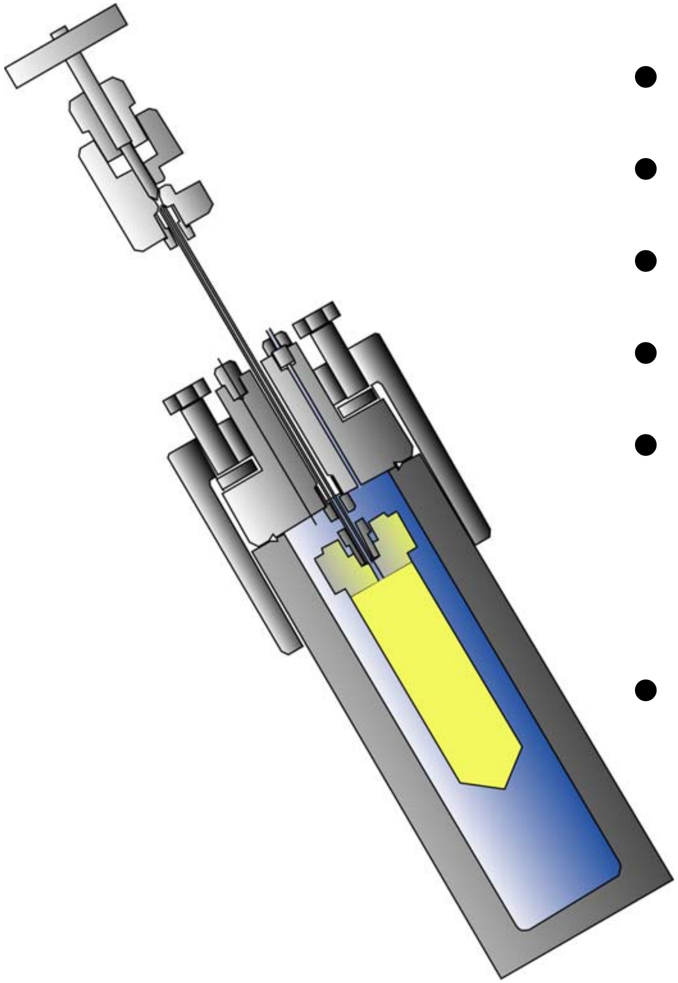
- **Effects on clay minerals and other silicates during and after diagenesis.**

- **Origin and distribution of carbonate cements and veins in sedimentary basin sandstones.**

- **Petrogenesis of carbonate veins in ore deposits**

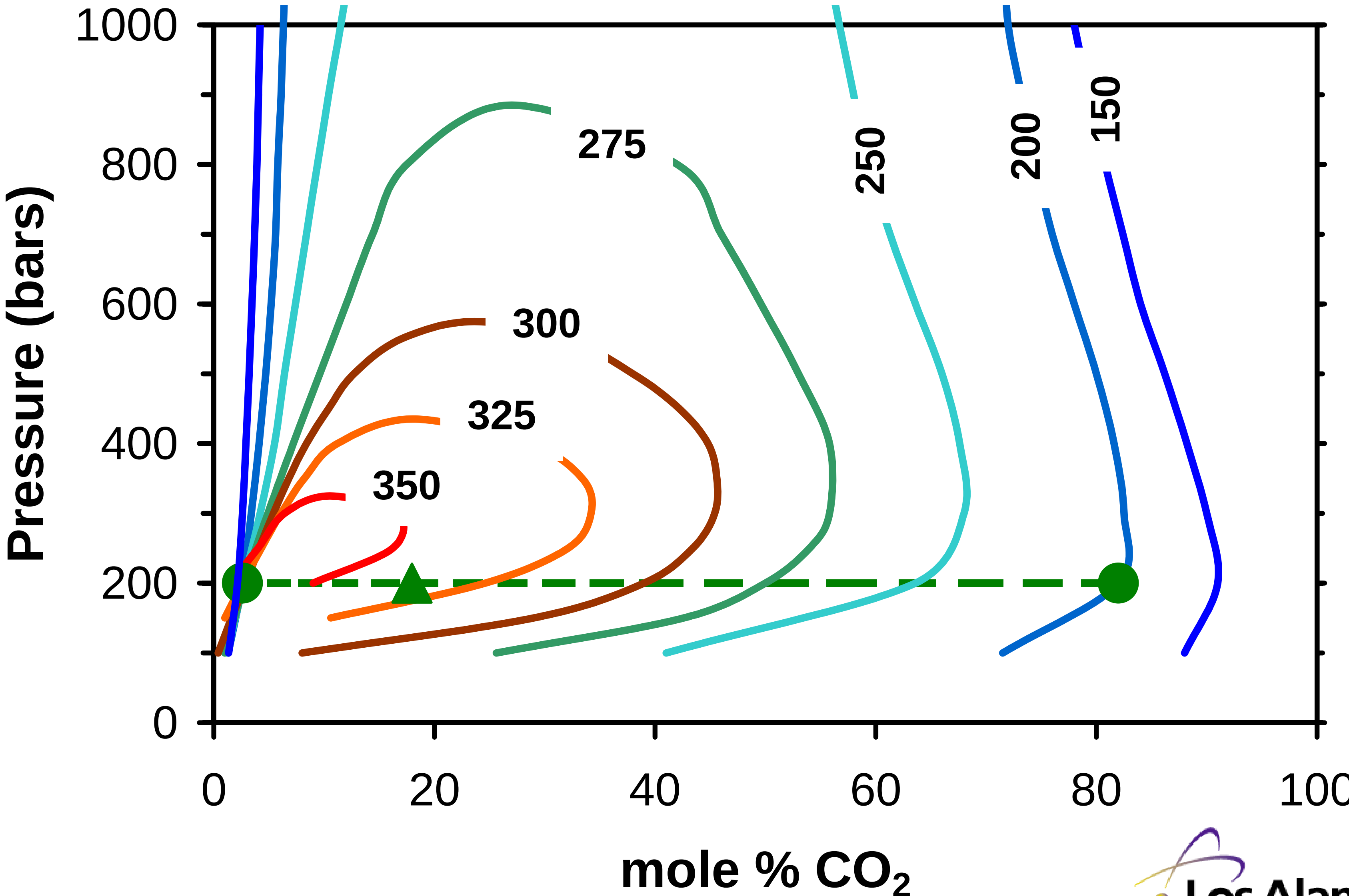
- **Silica cement in sandstones and quartz growth in veins**

Experimental Approach

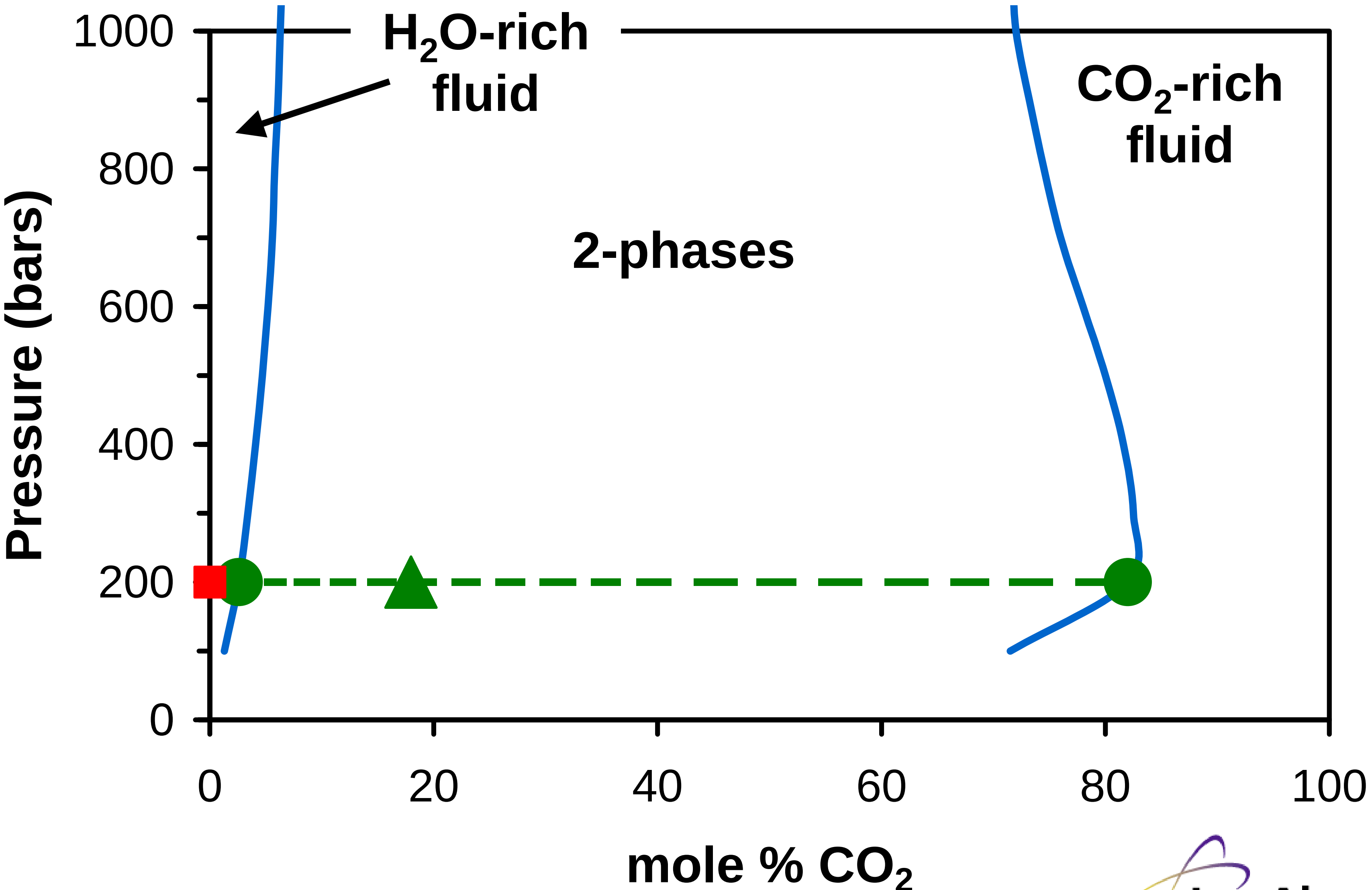


- **Flexible cell hydrothermal apparatus**
- **200°C and 200 bars**
- **5.5 molal NaCl brine**
- **Aquifer = model arkose**
- **Aquitard = argillaceous shale**
- **Experiment**
  - **Brine + rock for 32 days**
  - **Inject CO_2 into ongoing reaction, 45 days**
- **Control Experiment**
  - **Brine + rock for 77 days**

Phase Compositions, System H_2O-CO_2



Phase Compositions at 200°C



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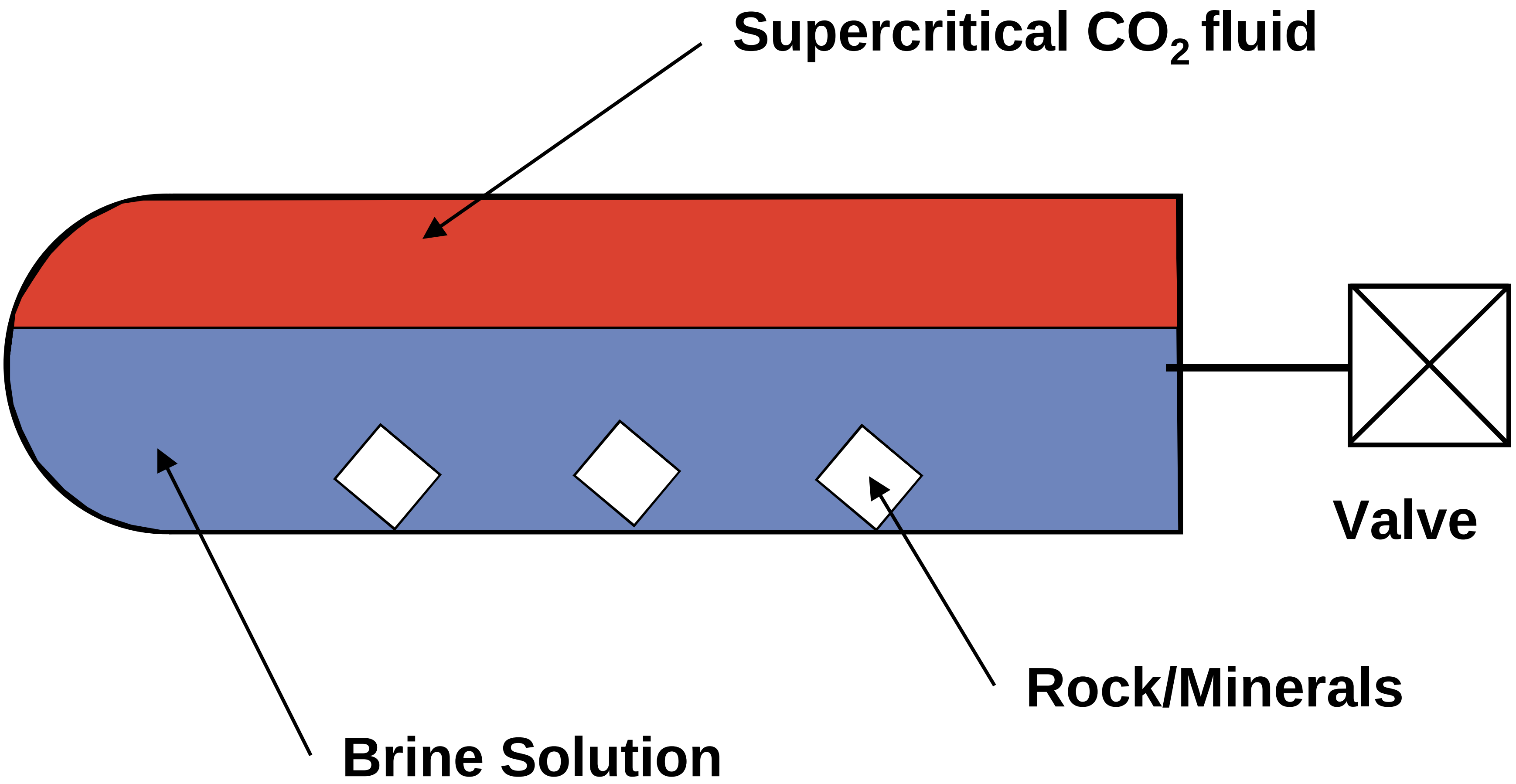
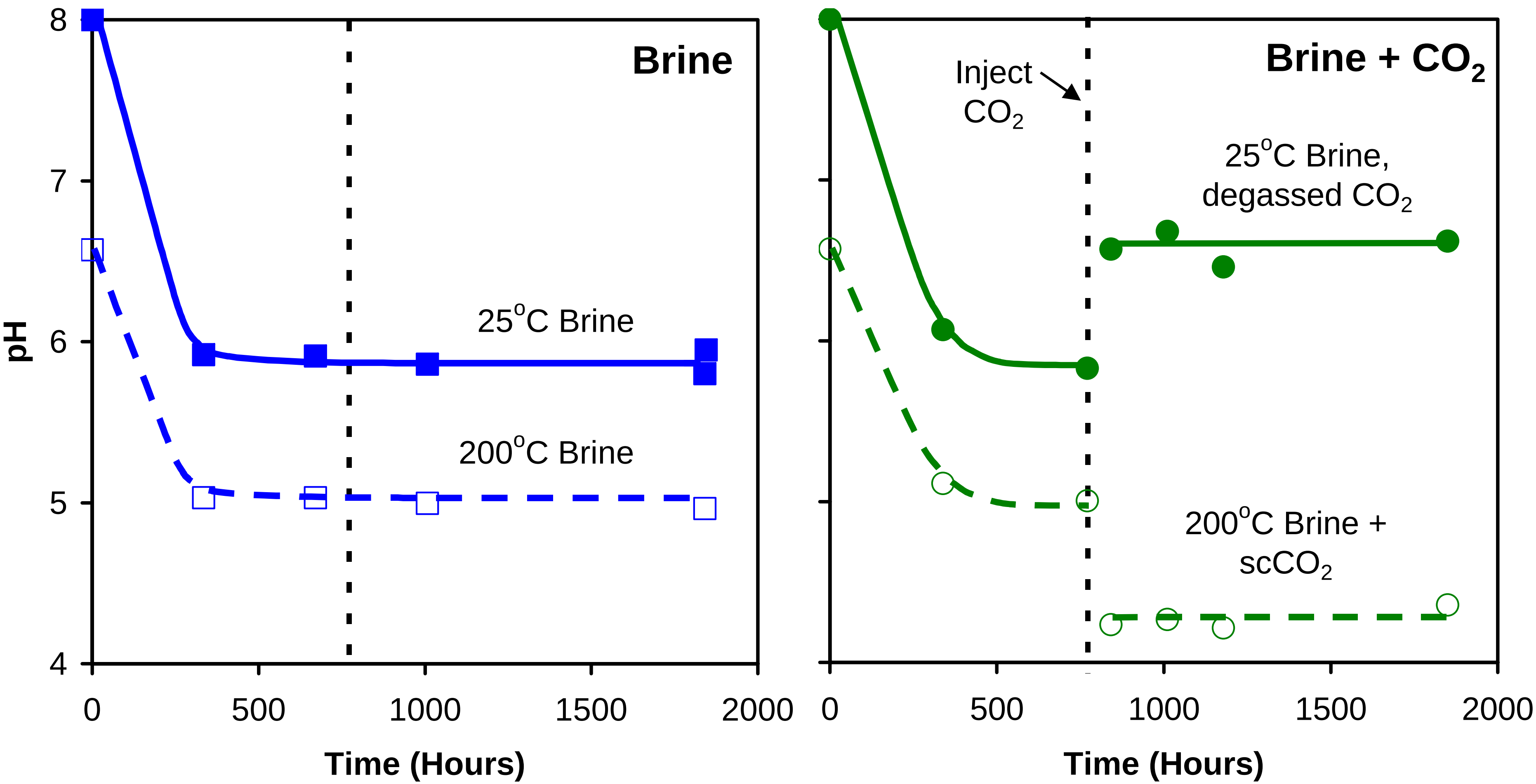
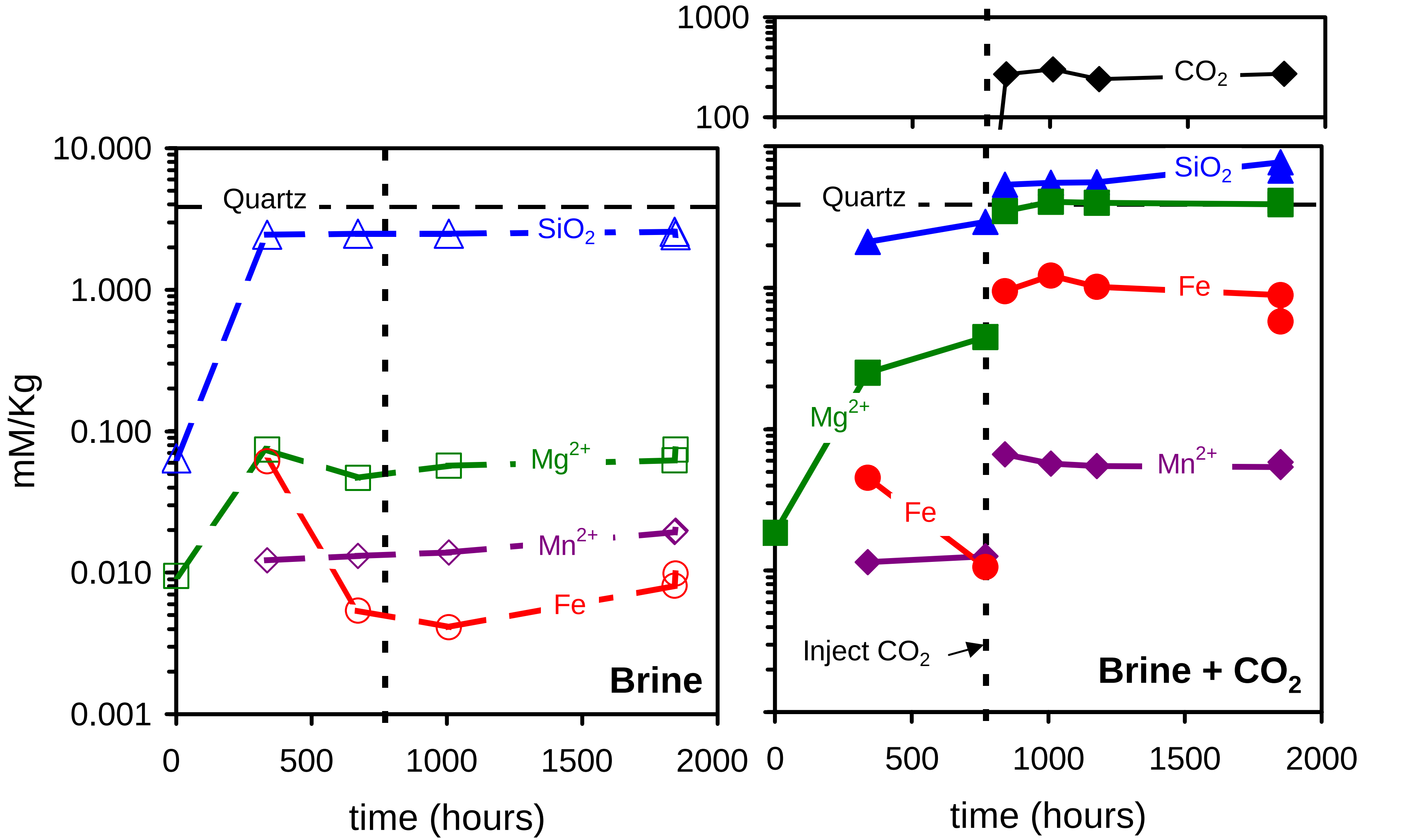
Experimental Approach



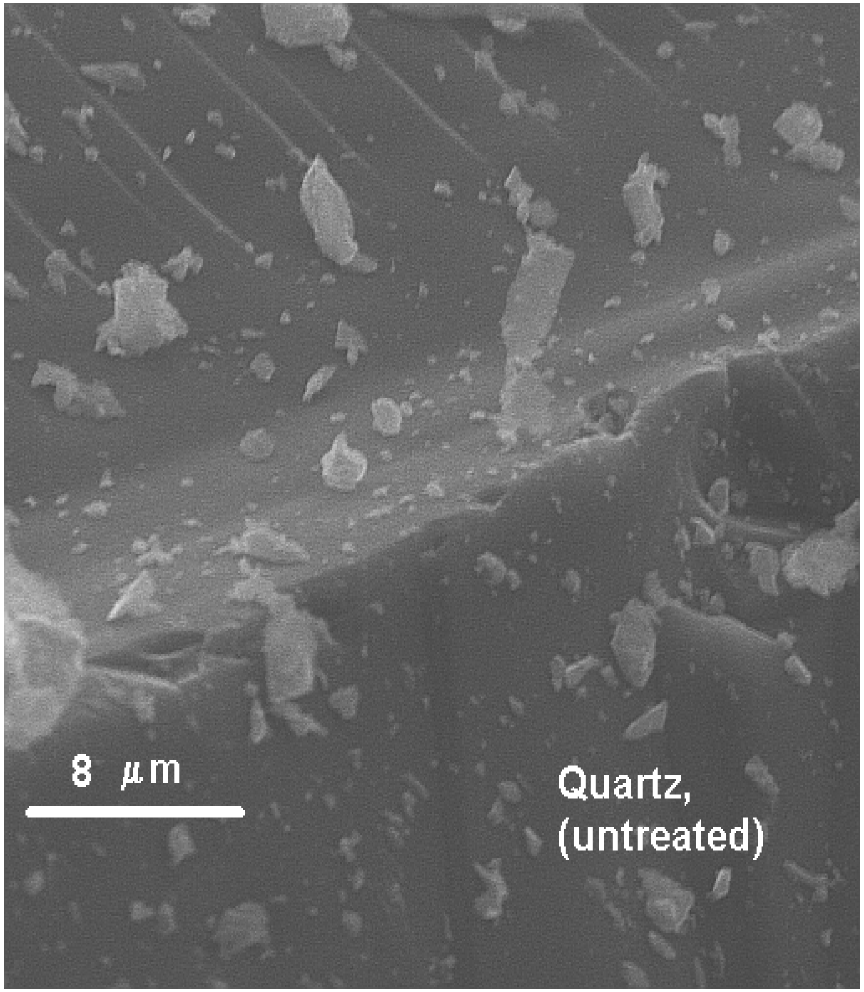
Brine Chemistry - pH

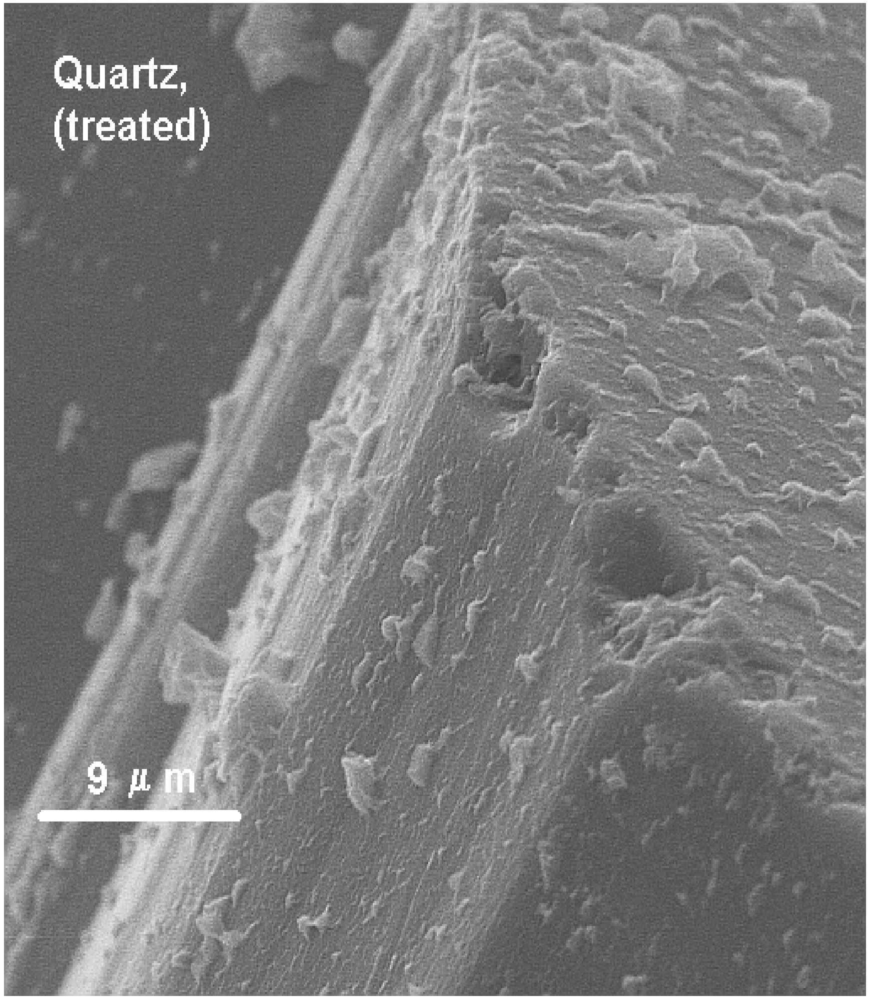


Brine Chemistry – Other Cations and CO_2

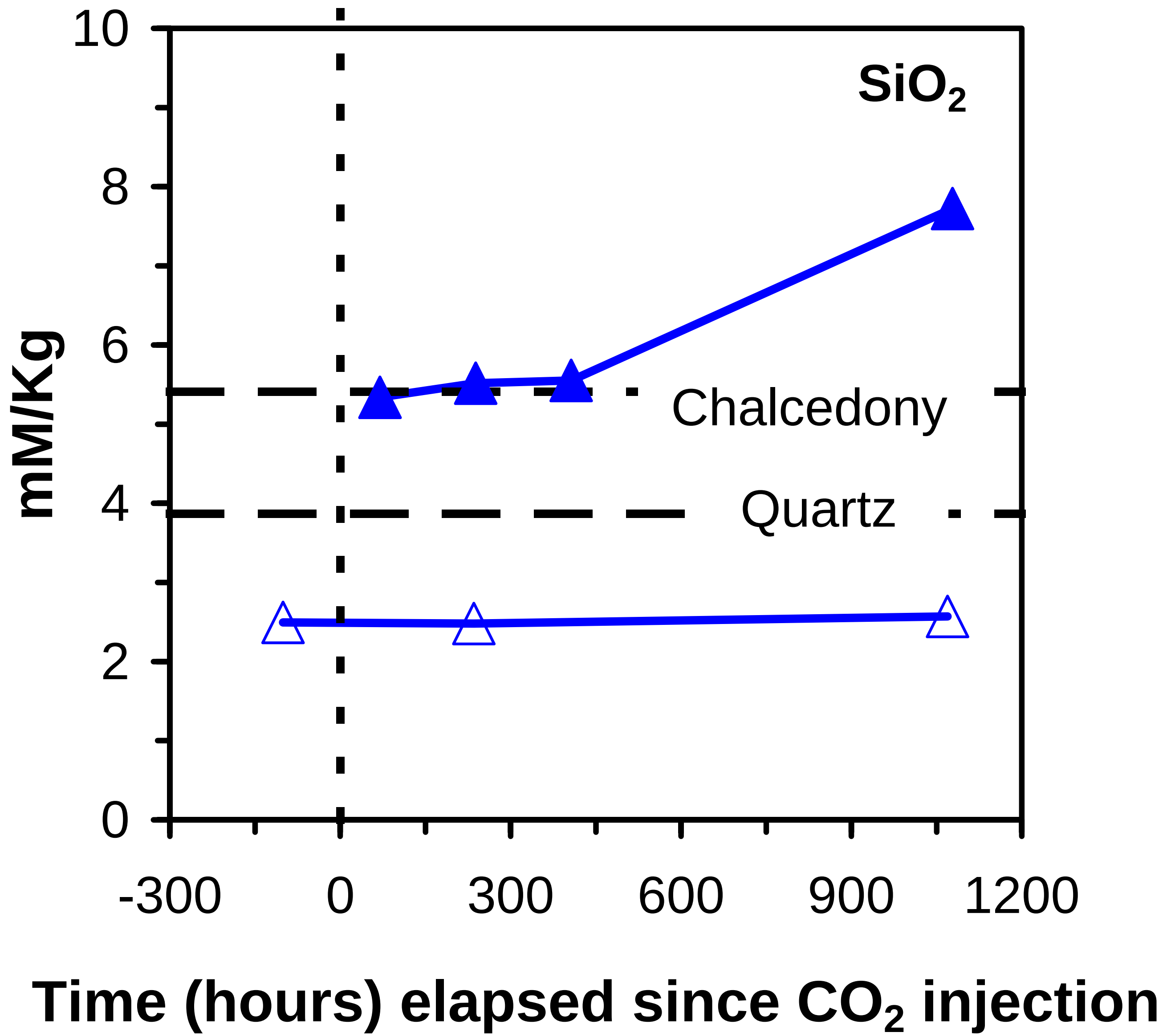


Quartz

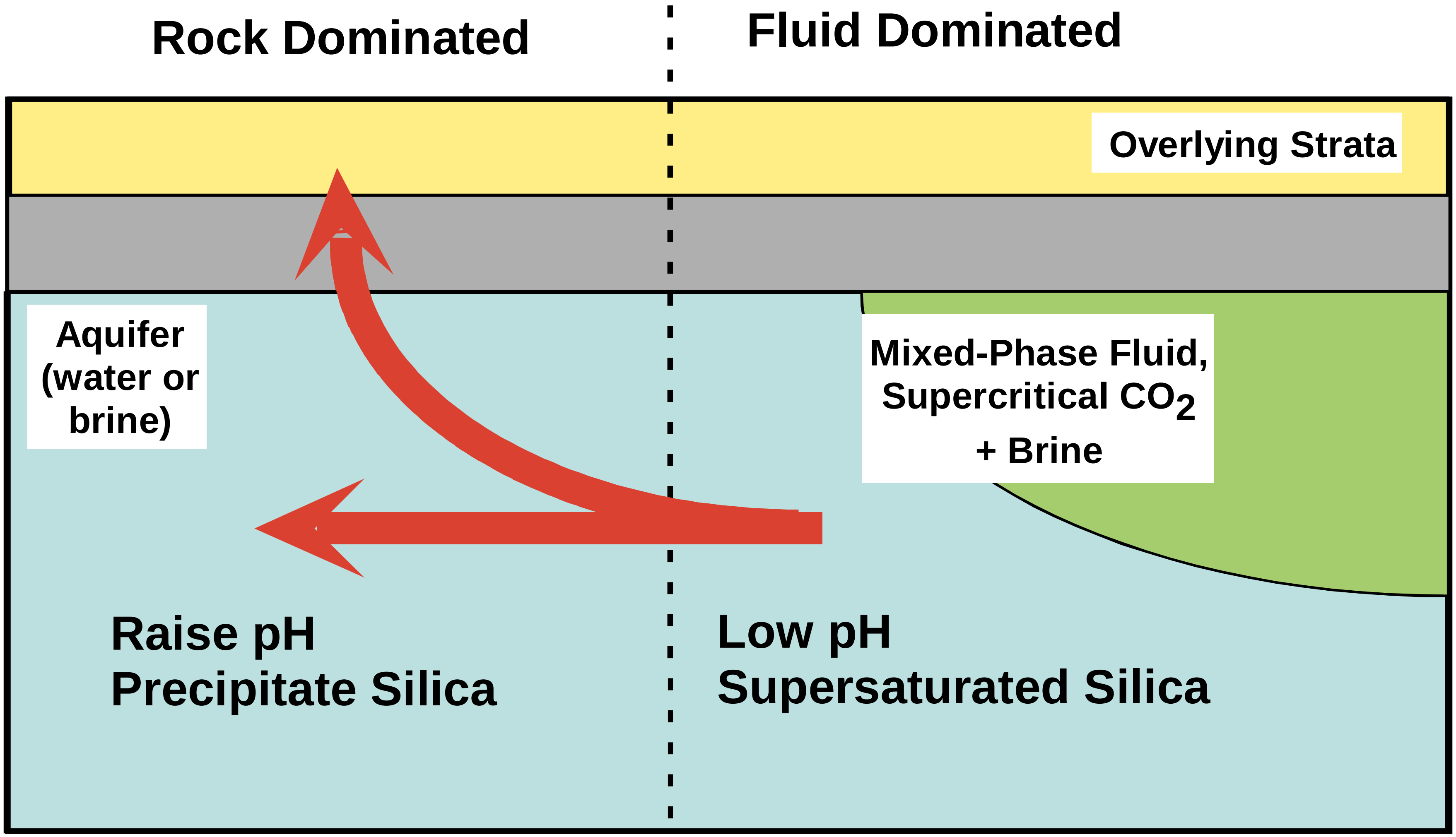




Brine Chemistry –Silica



Conclusions



Conclusions

- Conceptual and detailed geochemical reactions in mixed CO_2-rich and brine solution systems are only beginning to be explored
  - Reaction trends and kinetics of silicate reactions in the presence of mixed brine and CO_2-rich fluids can be characterized
  - Isotopic behavior is unexplored
  - Fluid inclusions from a wide range of natural systems should be re-examined

Applications and Acknowledgements

- Applications
  - Silica veins and cements
  - Low-grade metamorphism
  - Geologic CO_2 sequestration
  - Petroleum CO_2 flood recovery systems

- Acknowledgements
  - US DOE BES Geoscience Program
  - Los Alamos National Laboratory
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Multi-phase equilibrium relationships between supercritical CO2 and brine-rock systems may provide a source of silica cement in sandstones and quartz growth in veins. To investigate, experiments were conducted in a flexible cell hydrothermal apparatus at physical-chemical conditions of the shallow crust. A synthetic arkose (microcline + oligoclase + quartz + biotite) plus argillaceous shale were reacted with 5.5 molal NaCl brine. The system was held at 200 C and 200 bars for 32 days to approach steady state, then injected with CO2 and allowed to react for an additional 45 days. In a parallel experiment, the system was allowed to react for 77 days without injection of CO2. Trace ions initially absent from NaCl brine appeared in solution at mM (K, Ca, and SiO2) to uM (Mg, Al, Fe and Mn) quantities, reflecting reaction of brine with rock. Without CO2 injection, the SiO2 concentration (2.4 mM) was stable below calculated quartz solubility (3.9 mM). Injection of CO2 resulted in decreased pH (1 unit) and increased SiO2 concentration to a level near calculated chalcedony solubility (5.4 mM).

In the experimental system containing acidic brine and supercritical CO2, SiO2 concentrations were doubled by dissolution of silicate minerals and apparent concomitant inhibition of the precipitation of quartz (and other silicates). Evaluation of the mixing of hot hydrothermal solutions with ambient seawater at mid-ocean ridge vents (Janecky and Seyfried, 1984) also noted silica super-saturation and inhibition of quartz precipitation. These phenomena were attributed to kinetics of silica polymerization and precipitation under acid pH conditions, assumptions consistent with recent experimental results (Icopini et al., 2002). Return of silica super-saturated brine into a rock-dominated reaction system buffered to more neutral pH conditions may enhance precipitation of quartz, chalcedony, or amorphous silica as veins or cements, depending on the permeability structure of the host rock. Similarly, loss of CO2 or phase separation with decreasing pressure can substantially shift pH and result in massive vein or scale formation.

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